The "Two" Woodward-Hoffmann Rules

It was never obvious to me[1] (maybe it is to you) that the two common statements of the Woodward-Hoffmann rules are equivalent. The following is a pedantic but (hopefully) rigorous demonstration of the equivalence of these formulations.[2]

Proposition 1. *The following formulations of the Woodward-Hoffmann rules are equivalent:*

A) If the sum of the number of suprafacial $4q+2$ components and antarafacial $4r$ components of a pericyclic reaction is odd then it is thermally allowed; otherwise the reaction is thermally forbidden.

B) If the total number of antarafacial components of a $4n+2$ electron pericyclic reaction is even or the total number of antarafacial components of a $4n$ electron pericyclic reaction is odd, the reaction is thermally allowed; otherwise it is thermally forbidden.

We prove these two statements are equivalent by first restating them in mathematical terms.

We can associate a k-component pericyclic reaction with a set of ordered triples $\{(n_1, p_1, 1), \cdots, (n_k, p_k, k)\}$ by associating component i with ordered triple (n_i, p_i, i) using the following rules:

$$n_i = \begin{cases} 0 & \text{if } i \text{ is a } 4r \text{ component} \\ 1 & \text{if } i \text{ is a } 4q+2 \text{ component,} \end{cases}$$

and

$$p_i = \begin{cases} 0 & \text{if } i \text{ is suprafacial} \\ 1 & \text{if } i \text{ is antarafacial.} \end{cases}$$

Examples:

(1) The conrotatory 4 e^- ring opening of cyclobutene (${}_\sigma 2_a + {}_\pi 2_s$) is associated with $\{(1,1,1),(1,0,2)\}$.

(2) The Diels-Alder reaction (${}_\pi 2_s + {}_\pi 4_s$) is associated with $\{(1,0,1),(0,0,2)\}$.

(3) The Alder ene reaction (${}_\pi 2_s + {}_\sigma 2_s + {}_\pi 2_s$) is associated with $\{(1,0,1),(1,0,2),(1,0,3)\}$.

(Note that the i's are merely counters used to distinguish components. The value of i assigned to a given component is arbitrary.)

We can restate the condition in formulation A as "if the sum of the number of $(1,0,i)$ and $(0,1,i)$ components is odd," or equivalently, "if the number of components with $n_i \neq p_i$ is odd."

To restate formulation B, we first observe that the total electron count of the pericyclic reaction is of the form $4n+2$ when the number of $4q+2$ components is odd and $4n$ when the number of $4q+2$ components is even. Thus we can restate the condition in formulation B as "if $\sum_{i=1}^k n_i$ is odd and $\sum_{i=1}^k p_i$ is even, or vice versa," or more succinctly, "if $\sum_{i=1}^k n_i + p_i$ is odd."

The following is now equivalent to Proposition 1 in our new notation.

Proposition 2. *Let $S = \{(n_1, p_1, 1), \cdots, (n_k, p_k, k)\}$ be a set of ordered triples with all $n_i, p_i \in \{0, 1\}$, and $T = \{(n_i, p_i, i) \in S | n_i \neq p_i\}$. Then $|T|$ and $\sum_{i=1}^k n_i + p_i$ have the same parity.*

Proof. We note the any element of S with $n_i = p_i$ can be omitted without changing the parity of $\sum n_i + p_i$, since $n_i + p_i = 0$ or 2. In other words, $\sum_{i=1}^k n_i + p_i \equiv \sum_{x \in T} n_i + p_i \pmod 2$. But the elements in T satisfy $n_i + p_i = 1$, so $\sum_{x \in T} n_i + p_i = \sum_{x \in T} 1 = |T|$. Thus $|T| \equiv \sum_{i=1}^k n_i + p_i \pmod 2$, i.e., they have the same parity, as claimed. □

It is readily apparent that the parity of $|T|$ and $\sum_{i=1}^k n_i + p_i$ correspond to thermally allowed (odd) and thermally forbidden (even) pericylic reactions in formulations A and B, respectively. We showed that they always agree, and hence, we conclude that formulations A and B of the Woodward-Hoffmann rules are equivalent.

[1] ymw, last modified 2010/10/23

[2] Formulation A was proposed by Woodward and Hoffmann in *ACIEE* **1969**, *8*, 781-853, while formulation B is essentially equivalent to the Dewar-Zimmerman Hückel-Möbius aromatic transition state approach.